Chapter-1

Introduction and Literature review

CHAPTER 1: Introduction and Literature Review

1.1 Energy Scenario

The consumption of energy is an important issue that is gaining boosted focus all around the globe. The population is increasing worldwide day by day, so is our necessity for energy[1]. The utilization of energy in India for the last 30 years is exemplified in figure 1.1. On a large scale, for accomplishment of the demand of the energy, we are relying on non-renewable sources. According to the Global energy statistical yearbook 2021, 74% of the world's energy demand and 81 % in India are fulfilled by non-renewable energy sources. The significant dependence on fossil fuels has a massive impact on the environment. Global warming, depletion of the ozone layer, and climate change are extensive environmental concern. In the last two decades, demand for primary energy is grown by 49% (annual increment of 2%), leading to the emission of CO_2, which has increased by 43% with a yearly increase of 1.8%[2]. Generating power without harming the environment is a task that compels the scientific community to search for alternative energy sources which are cost-effective, efficient, and have low environmental threatening gaseous emissions. These challenges establish that renewable energy sources will play a significant role in the satisfying present and future energy needs to meet the worldwide increase in energy demand, particularly for ecofriendly energy supply[3].

Several renewable energy technologies are being established in recent years, such as Solar energy, Bioenergy, Hydropower energy, Wind energy, and geothermal energy[4]. However, all these renewable sources have their constraints and limitations. The efficiency of systems (solar panel has about 22% of efficiency in its most advanced system or a windmill

is not much helpful for a power plant of diesel truck), Specific regions for setting up (open windy fields for wind energy), intermittency of energy supply (solar panel does not provide power at night) are some interruptions due to which it is better to look towards other energy sources, which are clean and green along with having high efficiency. A part of the research is concentrating on electrochemical devices, which can produce green energy with high efficiency. Among all possible devices, Fuel cells are the prominences as a reliable source of electricity if the fuel is delivered constantly. Unlike other renewable energy sources, it can be easily relied on as a sole power source [5]. Fuel cells are electrochemical devices that produce electricity with low environmental impact and great efficiency by converting fuel and oxidizer into products through electrochemical reactions. Fuel cells can serve as primary as well backup power sources [6], [7].

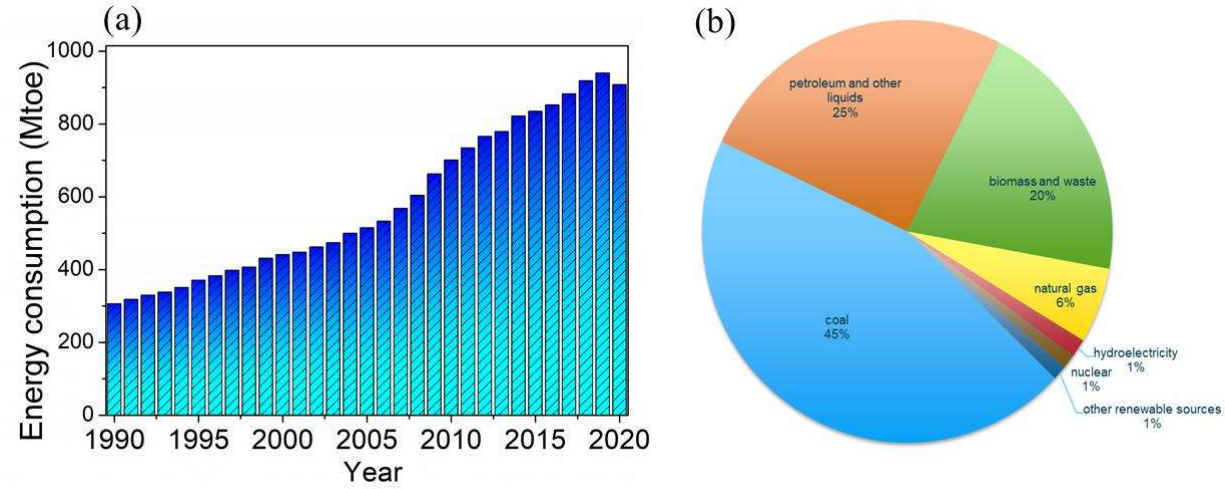

Figure 1.1: (a) Total energy consumption in India from 1990 to 2020. (b) Breakdown of energy by various sources globally[8].

1.2 Fuel Cells: An Overview

Fuel cells are energy conversion device that uses an electrochemical reaction with a controlled flow of electrons to convert chemical energy of fuels into electrical energy, with water as a byproduct. Fuel cells combine the best properties of an engine and a battery, and they can function as long as fuel is supplied, much like an engine. Their traits are identical to a battery under load conditions[9]. All fuel cells have the similar basic structure, an electrolyte, and two electrodes (cathode and anode). Fuel cells typically use compressed hydrogen as fuel and oxygen (from the air) to sustain the chemical reaction. The scientific community has well-known about fuel cells for over 150 years. William Nicholson and Anthony Carlisle defined the electrolysis process in 1800, in which water is broken down into hydrogen and oxygen using electricity[10]. Sir Humphrey Davy successfully validated the first-ever concept of a fuel cell in 1801[11]. This was followed by the groundbreaking work of Prof. Christian Friedrich Schőnbein, who discovered the fuel cell's principle in 1838 [12]. Sir William Robert Grove, a British physicist, chemist, and lawyer, is extensively recognized with developing the first fuel cell in 1839 based on the reverse electrolysis of water [13]. While investigating coal gas fuel cells in 1899, scientist Ludwig Mond and his colleague Charles Langer coined the name "fuel cell." They reached 6 mA/cm^{-2} (electrode area) at 0.73 volts using electrodes made of thin, perforated platinum[14]. Friedrich Wilhelm Ostwald, one of the originator of physical chemistry, experimentally defined the functions and interconnections of various fuel cells in 1893[12]. Fuel cell development has speeded up rapidly since the early 1990s due to the commercialization of various applications. Fuel cell applications may be divided into three categories: Stationary power generation[15], [16], Portable power generation[17], and power for transportation[18].

1.2.1 Design and working of Fuel Cell

An anode, a cathode, and an electrolyte membrane consist of the fundamental physical structure of a fuel cell. There are several kinds of fuel cells, and their operation is a bit different from each other, but their basic geometrical features remain the same. In general terms, the reaction between hydrogen and oxygen generates the electricity in a fuel cell. Fuel (usually hydrogen) is passed through the anode of a standard fuel cell, while oxidant (usually oxygen from the air) is continuously supplied to the cathode side. On the anode side, hydrogen split into hydrogen ions and electrons. The ion moves from the anode to the cathode via the electrolyte, whereas the electron moves through the external circuit, causing in direct current. At the cathode end, ion-electron and oxygen combine to yield the water molecules as a by-product (Proton-conducting fuel cell). In some fuel cells, the electron is picked up by oxygen, and oxygen ion passes through the electrolyte to the anode, where it react with hydrogen ions (Oxide ion-conducting fuel cell)[19]–[21].

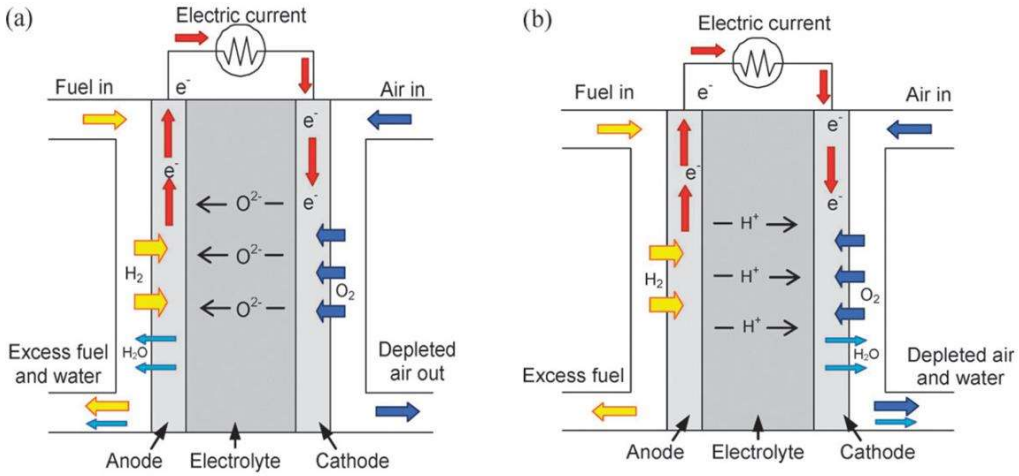

Figure 1.2: Schematic diagram of a fuel cell (a) Oxide ion conducting electrolyte and (b) Proton conducting electrolyte

Fuel cell efficiency is not restricted by any thermodynamic constraint, such as Carnot efficiency[22]. It happens because there is not any intermediate step of mechanical work and generally production of heat is prevented in case of fuel cell. It produces electrical energy more efficiently compared to traditional devices like combustion engines. Conventional techniques involve the conversion of fuel to heat, mechanical work, and then electrical power, and are usually limited to low efficiency of nearly 30%. Fuel cell bypasses the intermediate energy losses and produces electrical energy with higher efficiencies greater than 50%[23]–[25]. The fundamental working of the fuel cell may not be challenging to demonstrate but building an efficient and reliable fuel cell is far more complex. The voltage of a unit fuel cell is around 0.7 V[26]. Many cells must be connected in series to obtain a larger voltage and current. Such a collection is referred to as a "fuel cell stack" or simply "stack."' To overcome the voltage drop during a stack, 'bipolar plate' is used for cell interconnection. It connects the anode of one cell to the surface of the next cell's cathode. Apart from the stack, several other subsystems and components are also required; they are referred to as balance of plant (BoP). BoP, when coupled with the stack, forms a functional fuel cell system[27].

1.2.2 Type of Fuel Cell

Based on the use of electrolyte, the fuel cells are often sorted by operating temperature. This classification also establishes the mandatory fuel, the kind of electro-chemical reaction taking place, the type of catalyst, and other factors. This classification, in turn, affects the application for which these are most appropriate. Six types of fuel cells have emerged as visible systems for the present and near future[28]. Basic information and their comparison are listed in table 1.1.

The commercialization of fuel cells deals with two major tasks: improving durability and reducing the costs. The production of hydrogen is the most difficult challenge for cost-effective commercialization. Since the last decade, lots of research has been performed on all sorts of fuel systems. The Solid oxide fuel cell (SOFC) has the most prolonged development period, starting from the late 1950s. SOFC has attracted much research interest throughout the world in recent years for its potential market competitiveness, including high efficiency, fuel flexibility, low price, and long-life expectancy. The current focus of SOFC research is on the identification and synthesis of novel materials that can lower SOFC manufacturing cost and extend their lifetime. The reduced price will boost the production of SOFC and make it a sustainable substitute of traditional power technologies[29]–[32].

1.3 Solid Oxide Fuel Cell (SOFC)

SOFC is an essential energy conversion device that produces electricity through electrochemical reactions at high temperatures (600-1000 °C) by combining fuel and an oxidant over an ion-conducting oxide electrolyte. SOFC employs the solid ceramic material as an electrolyte. The high operating temperature of SOFC improves the reaction kinetics, which removes the need for any metal catalyst. SOFCs have substantial efficiency benefits over current thermally generated electricity technologies[29], [33], [34]. SOFC systems alone are up to 50 - 55% efficient, and, in combination with heat regeneration and cogeneration technologies, the overall efficiency can be lifted to 70 - 75%. Pollution levels are noticeably reduced with 20 - 40% CO_2 levels per kW of electricity produced. There are also reductions by 1 - 2 orders of magnitude in the nitrogen and Sulfur-based gases responsible for acid rain and other deteriorating health conditions. Furthermore, SOFC system efficiencies can be improved by the internal reforming of natural gas within the fuel cell stack. With modular

construction, it is likely to adapt SOFC systems to match the load requirement and, if fuel is present, the SOFC can run persistently in almost any environment.

Fuel cell type	**Mobile ion**	**Operating temperature**	**Fuel supplied**	**Application and notes**	**Efficiency**
Alkaline Fuel Cell (AFC)	OH^-	65-220 °C	Hydrogen or NH_3	Space vehicle	50-55 %
Proton Exchange Membrane Fuel Cell (PEMFC)	H^+	40-100 °C	Liquid ethanol	Vehicle and mobile application, for lower power CHP system	50-55 %
Direct Methanol Fuel cell (DMFC)	H^+	20-90 °C	Methanol	The portable electronic system of low power	30-40 %
Phosphoric Acid Fuel Cell (PAFC)	H^+	160-220 °C	Hydrogen	Power plants of up to 200 KW	40-50 %
Molten Carbonate Fuel Cell (MCFC)	CO_3^{2-}	600-800 °C	Hydrogen, CO, Natural gas, or propane	Suitable for medium to large CHP system, up to MW capacity	45-50 %
Solid Oxide Fuel Cell (SOFC)	O^{2-}	500-1000 °C	Natural gas or propane	Suitable for all sizes of CHP system, 2KW to multi-MW	45-60 %

Table 1.1: Comparison of different types of Fuel Cell

1.3.1 The basic operation of SOFC

A SOFC is made up of dense, oxygen ion-conducting electrolyte placed between two porous electrodes (cathode and anode). In solid oxide, fuel cell oxygen ions are conducting species. Oxygen supplied at the cathode end is reduced to oxygen ion (O2-), diffuses into the electrolyte, and transfers to the other side of the anode. This oxide ion reacts with the fuel at the anode side, giving up electrons and producing byproducts and heat. The interconnect is used to transport the electron through an external circuit. The electrochemical reactions that are associated with hydrogen fuel in SOFC are represented as:

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \text{ (At cathode end)} \quad (1.1)$$

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \text{ (At anode end)} \quad (1.2)$$

The overall reaction can be written as:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad (1.3)$$

The corresponding Nernst equation for this reaction will be:

$$E = E^0 + \frac{RT}{2F}\ln\left(\frac{PH_2PO_2^{1/2}}{PH_2O}\right) \quad (1.4)$$

Where E denotes the cell potential (or Nernst Potential), E_0 is the standard potential at unit activity, R is ideal gas constant, T is temperature, F is Faraday constant and PH_2, PO_2 and PH_2O is the partial pressure of hydrogen, oxygen and water respectively.

1.3.2 Components of SOFC

The SOFC comprises different components like cathode, anode, electrolyte, interconnects, materials for sealing, and fuel distribution system. Some several criteria and properties need to be possessed by each material to operate in a different capacity. The SOFC components, along with their requirement, are mentioned below:

1.3.2.1 Electrolyte:

In SOFC, the electrolyte has a task to conduct the oxide ion from cathode end to anode end. As the name itself said, SOFC uses solid oxide ion conductors as electrolyte material. In electrolytes, oxide ion conduction occurs via a thermally activated oxygen vacancy hopping mechanism. The main prerequisite for the electrolyte materials is:

- Sufficient oxide ion conductivity (>0.1 S/cm at operating temperature) without any significant electronic conductivity.
- Fully dense with no open porosity
- Compatibility of Thermal expansion coefficient (TEC) with another component of the cell.
- Electronic transference number should be low ($< 10^{-3}$)
- Chemical and thermodynamic stable over a wide range of temperature (RT to 1000 °C) over a wide range of oxygen partial pressure ($1\text{-}10^{-22}$ atm)
- It should be Chemical inert towards cathode and anode.
- Negligible evaporation
- It should have reliable mechanical properties (such as facture strength should be greater than 400 MPa)

1.3.2.2 Anode:

The primary objective of an anode is to provide a place for the reaction of oxide ions with the gas fuel. The anode material of SOFC must comply with the following requirement:

- High electronic activity
- High electrocatalytic activity

- High porosity for mass transport of reactant and product gases
- Comparable thermal expansion coefficient with electrolyte
- Good microstructural strength to operate SOFC at working temperature
- Stable under the reducing atmosphere of fuel.
- It should be able to handle a variety of fuels and not react with the SOFC's commonly used fuel.
- It must resist the action of byproduct (H_2O) (especially metal anode)

1.3.2.3 Cathode:

In a solid oxide fuel cell, the reduction of oxygen occurs at the cathode end. To serve the better, the cathode material in SOFC has needed to be fulfilled the following requirements:

- High electronic conductivity (preferably greater than 100 S/cm in an oxidizing atmosphere is preferable)
- Enough porous for fast diffusion of molecular oxygen from cathode to cathode/electrolyte interface.
- High catalytic activity for oxygen reduction reaction (ORR).
- The thermal expansion coefficient (TEC) needs to be matched with the other component of the cell.
- Good chemical and dimensional stability during cell operation and fabrication of interconnection, and fuel electrode layers.
- Good chemical compatibility with electrolyte and interconnect materials as well minimum interaction with electrolyte.

1.3.2.4 Interconnect:

The interconnection is the connection between the adjacent cell in the SOFC stack. It connects the cathode of one cell to the anode of the next cell through an electrical connection. It also serves as a physical hurdle between the oxidizing (at the cathode) and the reducing (at the anode end) atmosphere. The interconnect material must fulfill the following selection benchmarks for proper SOFC operation:

- Electrical conductivity of nearly 100% with area-specific resistance (ASR) less than $0.1\Omega\ cm^{-2}$.
- Structural, chemical, and phase stable at the extreme operating environment of SOFC in reducing and the oxidizing atmosphere.
- Non-reactivity towards electrode and electrolyte material.
- Matching Thermal expansion coefficient with the other component of the cell.
- Moderate mechanical strength.
- Low permeability for hydrogen (fuel) and oxygen to avoid the direct combination of oxidant and Fuel.

1.3.2.5 Sealing materials:

The function of sealants material is to avoid any leakage of either fuel or air from their respective chamber of SOFC stacking. In some configurations, it also offers mechanical bonding of components as well in some designs, and it provides electrical insulation between the stack components. The sealing material needs to fulfill the following demand for the SOFC device to function properly:

- It should have high hermeticity (i.e., no gas leak)

- The thermal expansion coefficient should be similar to the other cell component.
- Insulating in nature
- Long term chemical stability (>40,000 h) under oxidizing/wet fuel
- Enough toughness under external static and dynamic force.
- Chemical compatible with adjoining SOFC components.
- Admirable bond strength to prevent leakage, as well as compressive loading to support the stack load.
- Enough tolerance to thermal shocks.

1.4 Reaction and Kinetic mechanism for the cathode in SOFC

Since this research work is based on the cathode materials, therefore it is worthwhile to discuss the kinetics and chemical reactions taking place at cathode. The ORR takes place at the cathode end in SOFC, and the equation followed for the reduction is already mentioned in equation 1.1. However, this reaction is quite different from the other catalytic reactions in many ways. It is commonly assumed that a cathodic reaction can occur at the Triple phase boundary (TPB). TPB is defined as that site where oxide ion conductor, electron conductor, and gas-phase come together simultaneously. The illustration of TPB is shown in Figure 1.3. Although overall ORR looks very simple, the elementary steps associated with the ORR are quite Complex.

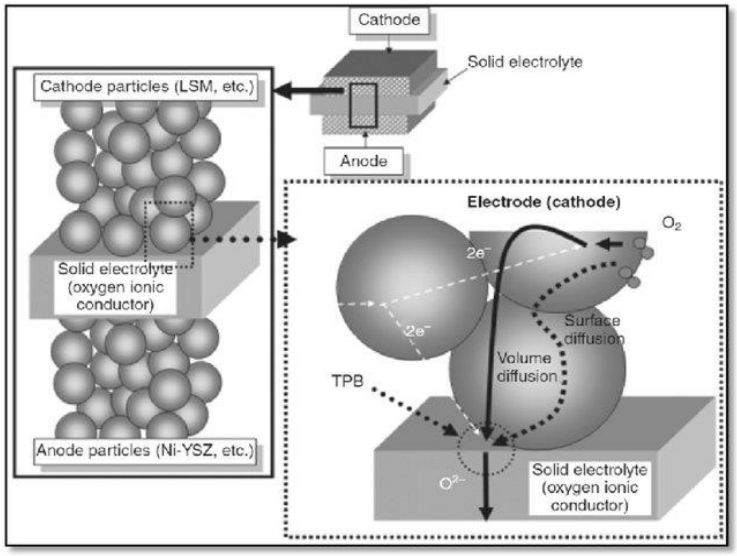

Figure 1.3: Schematic representation of Triple Phase Boundary[35]

1.4.1 Mechanism of Oxygen Reduction Reaction (ORR)

Single diatomic oxygen (O_2) must be transformed in some 'electroactive' state by one or more steps for the ORR to take place. The overall ORR reaction entails different bulk and surface step and can be divided into three key steps revealed as follows[36]–[38] :

(i) The reduction of oxygen molecules into oxide ions and their adsorption, dissociation, and incorporation into the cathode lattice.

(ii) Ionic transport through the cathode towards the electrolyte.

(iii) Jumping of oxygen anion into electrolyte site.

For SOFC cathodes, there are three possible pathways out of which cathodic reactions can occur (Figure 1.4)[39] :

1. **The Electrode Surface Path**: This path is appropriate in the case of the electronic conductor. This path includes diffusion of oxygen followed by the adsorption of oxygen and diffusion of dissociated oxygen (and partly ionized) along the surface

towards the TPB (Fig. 1.4 a) At TPB, complete ionization of oxygen species takes place and then ionic transfer into the electrolyte. Integration into the electrolyte doesn't require to occur directly at TPB. Broadening of the incorporation zone can be initiated via surface or interface diffusion of ionized oxygen.

2. **The Bulk Path**: This path is followed by a Mixed ionic-electronic conductor (MIEC). This path comprises of the diffusion and adsorption of oxygen gas on the cathode surface and the dissociation and ionization of oxygen into oxide ion, followed by the incorporation of ion into the cathode (Fig. 1.4 b). The electrode transport oxidized ion into the electrolyte.
3. **The Electrolyte Surface path:** This route is appropriate for the cases of the composite conductor. This pathway considers adsorption and ionization of oxygen species on the electrolyte surface followed by the migration of species through the electrolyte surface towards the TPB (Fig. 1.4 c). This path is identical to the electrode surface pathway from a geometrical point of view. However, in favor of the electrode surface pathway, this path is overlooked. An active zone for the cathodic reaction is confined very close to the TPB because of the low electronic conductivity of the most suitable electrolyte.

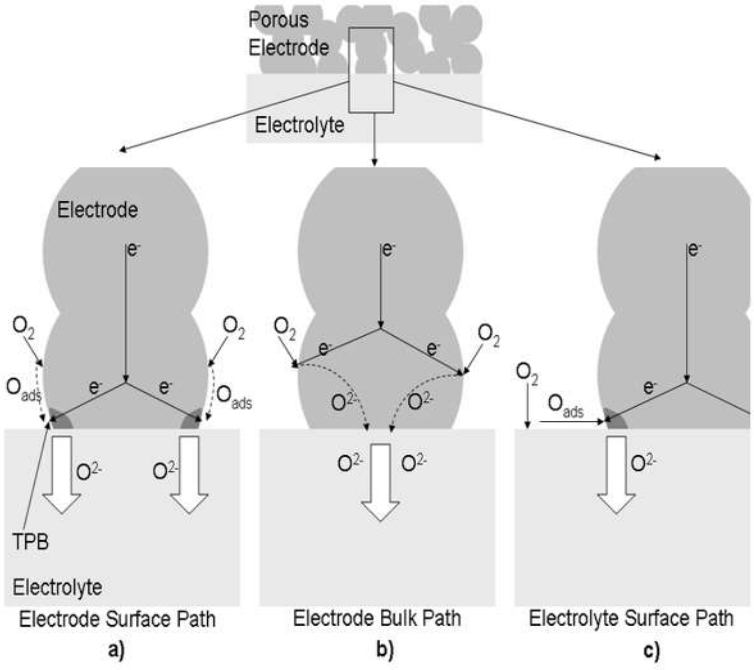

Figure 1.4: Schematic illustration of three reaction paths for the cathodic reaction [39]

The ORR can take place in any of the three paths mentioned above, and each path may have one or more elementary steps that are rate-defining step. It is not always possible to predict which elementary reaction is the rate-restricting step for ORR. The path which has the fastest rate-determining step will dominant the overall reduction reaction rate. To understand the rate-limiting step along with the dominant pathway, numerous studies have been employed, including various techniques such as cyclic voltammetry (CV)[40],[41], electrochemical impedance spectroscopy (EIS)[42],[43], isotope exchange depth profile (IEDP)[44], [45], steady Stade polarization[46] and actual fuel cell testing[47], [48]. These all studies provided crucial information regarding the element reaction occurring during the ORR. However, in this thesis, we focus only on CV due to the following reasons:

1. *CV is widely used to access the catalyst activity and is valuable for discovering the electrochemically active surface area (ECSA)*[49].
2. *CV can be used to acquire information about electrochemical reactions, including kinetics, mechanism of reactions, reversibility, and electrocatalytic process. Besides ORR, the application of this technique is also quite common in Oxygen evolution reaction (OER) and hydrogen evolution reaction. (HER)*[50].

1.4.2 Mechanism for Oxygen Evolution Reaction (OER)

OER is the core reaction of fuel cell to carry out its reversible process along with ORR. Besides fuel cell, OER plays vital role in several other energy system such as metal-air batteries, water electrocatalysis. The reversible reaction of OER is Hydrogen evolution reaction (HER). OER is heterogenous reaction and basically the half reaction of water splitting (eqn 1.5).

$$2H_2O \rightarrow 2H_2 + O_2 \qquad (1.5)$$

OER usually takes place at anode end whereas HER take place at cathode end. The mechanism of OER is different under different electrolyte medium (acidic or alkaline)[51]. All the steps involved in OER are thermodynamically uphill process, and the step with highest energy barrier become the rate-limiting step of OER[52]. The cathode and anode reactions in acidic and alkaline conditions are as follows:

1. Acidic Condition

(i) Cathode reaction:

$$4H^+ + 4e^- \rightarrow 2H_2 \qquad (1.6)$$

(ii) Anode reaction:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+ + 4e^- \qquad (1.7)$$

2. Alkaline condition

(i) Cathode reaction:

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \qquad (1.8)$$

(ii) Anode reaction:

$$4OH^- \rightarrow 2H_2 + 2H_2O_{(l)} + 4e^- \qquad (1.9)$$

The mechanism of OER (anode reaction) under acidic or alkaline medium proceed in four to five steps described in following equations:

- **For acidic environment:** The acidic mechanism involves the production or H^+ and e^- pairs.

$$M + H_2O \rightarrow MOH + H^+ + e^- \qquad (1.10)$$

$$MOH + OH^- \rightarrow MO + H_2O + e^- \qquad (1.11)$$

$$2MO \rightarrow 2M + O_2 \quad (1.12)$$

$$MO + H_2O \rightarrow MOOH + H^+ + e^- \quad (1.13)$$

$$MOOH + H_2O \rightarrow M + O_2 + H^+ + e^- \quad (1.14)$$

- For alkaline environment:

$$M + OH^- \rightarrow MOH + e^- \quad (1.15)$$

$$MOH + OH^- \rightarrow MO + H_2O \quad (1.16)$$

$$2MO \rightarrow 2M + O_2 \quad (1.17)$$

$$MO + OH^- \rightarrow MOOH + e^- \quad (1.18)$$

$$MOOH + OH^- \rightarrow M + O_2 + H_2O \quad (1.20)$$

Here M represent the active site in both cases.

1.5 Materials Selection for Cathode of SOFC

The selection of the cathode materials is crucial regarding SOFC. As a cathode, a wide range of materials have been investigated. These materials can be categorized widely in the category as mentioned below:

1.5.1 Magnetite based cathodes

Oxygen non-stoichiometry and defects have a considerable influence on the electronic and ionic transport properties of cathode materials. Lanthanum magnetite-based Oxides have either oxygen-deficient or excess non-stoichiometry. This is the most studied material, which

lies under this category[53]–[55]. The general formula is $Ln_{1-x}A_xMnO_{3-\delta}$, where A is a divalent cation. Most commonly, Strontium (Sr) is used as a dopant for Lanthanum magnetite because its size matches with lanthanum. Doping of Sr enriches the electron-hole concentration, which results in higher conductivity. However, the conductivity of Lanthanum magnetite based cathode lie between 200 S/cm to 300 S/cm[56], [57], and also the electrical properties of Lanthanum magnetite-based cathode are not fit for the temperature range below than 800 °C. For that, Lanthanum (La) can be substituted with the other rare earth elements. Sr doped $PrMnO_3$ revealed low overpotential, and its TEC is also compatible with Yttrium-based Zirconia (YSZ)[58].

The majority of the work in Lanthanum magnetite is focused on the doping on Sr-doped A-site. However, Ca doped Magnetite has also displayed good performance as cathode materials. $Pr_{0.7}Ca_{0.3}MnO_3$ showed chemically compatible, and its TEC is well-matched with YSZ, and also its conductivity lies to the close of Sr doped $PrMnO_3$[59].

As for the B-site doping, Scandium (Sc) is a favorite choice. The doping of Sc introduced the nonstoichiometric defect in the perovskite lattice of lanthanum magnetite, which increased the oxygen ion mobility. Sc doped magnetite $La_{0.8}Sr_{0.2}Mn_{1-x}Sc_xO_{3-\delta}$ is a potential cathode material for IT-SOFC[60]. However, the high cost of Sc is a concern in this category of cathode materials.

$Sr_{1-x}Ce_xMnO_{3-\delta}$ ($0.1 \leq x \leq 0.3$) system is another choice of cathode materials under this category. The TEC value of these cathode materials varies between 10.1×10^{-6} -12.6×10^{-6} K^{-1}, which lie close to the CeO_2 based electrolyte[61]. Doping of Cobalt on B-site lowers the Area Specific resistance (ASR) and enhances the catalytic activity. ASR of

$Sr_{0.8}Ce_{0.2}Mn_{0.8}Co_{0.2}O_{3-\delta}$ is 20 times lower than that of $Sr_{0.8}Ce_{0.2}MnO_{3-\delta}$ and has high catalytic activity for ORR at the temperature range of 700 °C - 800 °C[62].

1.5.2 Ferrite based cathodes

In ferrite-based cathodes, the mobility of electrons or holes is considerably higher than that of oxygen ions. As a result, the hole-conduction process directs the total conductivity of these cathodes. The reactivity of Ferrite based cathodes with YSZ is substantially reduced, and also, the TEC is lying close to the YSZ and CGO electrolytes. Lanthanum ferrite ($LaFeO_3$) is expected to remain stable because of the stable electronic configuration of Fe^{3+} ion ($3d^5$ configuration).

The addition of Sr to $LaFeO_3$ created charge unbalancing, maintained by forming Oxygen vacancy or Fe^{4+} ion. Sr-doped $LaFeO_3$ (LSF) cathodes exhibit promising power density and stability at 700 °C[63]. The ASR value of LSF can be reduced by incorporating La deficiency. ASR value of $La_{0.8}Sr_{0.2}FeO_3$ is reported as 0.1Ω cm^2 at 800 °C and TEC of $La_{0.75}Sr_{0.25}FeO_3$ closely matches with YSZ and CGO electrolyte[64].

Doping of Cu in lanthanum strontium ferrite improves the kinetic activity for ORR, and also copper doping reduces the sintering temperature for electrode fabrication[65], [66]. However, Cu-doped composition interact chemically with YSZ (above then 950 ^{0}C).

1.5.3 Nickelate based cathodes

Nickelate-based perovskite cathodes ($LnNiO_{3-\delta}$) are stable only below 1000 °C; further heating of these perovskites will lead to the K_2NiF_4- type structure. This transformation restricts the use of $LnNiO_{3-\delta}$ and can be employed by doping into Nickle sublattice[67].

Iron-doped nickelate ($LaNi_{1-x}Fe_xO_{3-\delta}$) exhibits high electronic conductivity, moderate TEC, and phase stability in air. $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF) has been explored as the option of cathode for IT-SOFC. The electric conductivity of LNF is reported at 580 S/cm at 800 °C [68]. However, LNF is more reactive towards the ZrO_2 based electrolyte rather than the conventional electrolyte.

Sr doped LNF (LNSF) is another choice of cathode under this category. The electrical conductivity of LNSF depends on the concentration of Ni/Sr and the temperature range. The highest electrical conductivity value in LNSF is achieved when the total concentration of Ni and Sr is about 0.6 at 600 °C[69].

1.5.4 Cobaltite based cathode

Cobalt-based cathode materials exhibit higher electronic and ionic conductivity than that of the other cathode materials. $LaCoO_3$ (LCO) has a high electronic density of states near the Fermi level (E_F). Sr doped LCO ($La_{1-x}Sr_xCoO_3$) has high oxygen diffusivity and high oxygen molecule dissociation ability, marking its electrode activity. However, a large amount of cobalt increases the TEC value. The significant value of TEC in cobalt-based perovskite is due to the formation of oxygen vacancy. Replacing lanthanum (La) with another rare earth elements (Pr, Nd, Sm, and Gd) can reduce the TEC and ASR. Among all rare earth elements, Pr^{3+} have the highest electronic conductivity and lowest overpotential because of the Pr^{3+}/Pr^{4+} valency change.

Doping of Cu in the Co site is anticipated to increase the catalytic activity and ionic conductivity. Although, the conductivity of Cu-doped LCO is less than LCO[70]. A combination of Pr, Sr on A-site and Cu, Co on B-site ($Pr_{0.7}Sr_{0.3}Co_{0.9}Cu_{0.1}O_{3-\delta}$) records the

maximum power density as 481 mW/cm^2 at 750 °C[71]. Besides Pr, Sr doped Samarium cobalt is another widely studied composition for cathode material. The electrical conductivity of this composition reaches up to 1000 S/cm at a temperature range of 800 °C - 1000 °C and shows metal-like behavior [72].

Mn doping on B-site along with the Sr doping on A-site also lowers the cathode overpotential. The lowest overpotential was observed in $Pr_{0.6}Sr_{0.4}Co_{0.9}Mn_{0.1}O_{3-\delta}$ among the tested $Ln_{0.6}Sr_{0.4}Co_{0.9}Mn_{0.1}O_{3-\delta}$ (Ln= La, Pr, Sm, and Gd). The electrical conductivity of $Pr_{0.6}Sr_{0.4}Co_{0.9}Mn_{0.1}O_{3-\delta}$ also reached 1400 S/cm at 500 °C[70].

1.5.5 Ferro-cobaltite based cathode

Lanthanum strontium cobalt ferrite is one of the primary cathode materials used for SOFC manufacturing. $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ (LSCF) has an excellent electrical conductivity, high oxygen diffusion coefficient, and high surface exchange coefficient. The TEC value of LSCF is also well matched with the frequently used electrolyte. The Sr concentration affects the ionic conductivity of LSCF at A-site, where electronic conductivity is influenced by the Fe and Co concentrations at B-site. LSCF based cathodes outperform LSM cathodes at lower temperatures. However, LSCF perovskite is generally incompatible with YSZ electrolytes. Substitution of Pr cation in the place La cation at A-site improves the cathode performance. The composition $Pr_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (PSCF) shows the highest conductivity, 1040 S/cm at 300 ^{0}C, and also ASR of PSCF-GDC(Gadolinium doped ceria) is 0.046 Ω cm^2 at 800 °C indicating that PSCF is promising cathode material[72].

Barium strontium cobalt ferrite has also been studied as a cathode material in SOFC using hydrogen as fuel. $Ba_{0.5}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (BSCF) cathode along with Samarium doped ceria

(SDC) electrolyte and NiO-SDC anode in a anode supported cell reached 1010 mW/cm^2 at 600 ^{0}C and ASR of this material is 0.055-0.071 Ω cm^2[73]. However, the TEC of BSCF is much higher, with a value of 20 x 10^{-6} K^{-1} in the temperature range 50-800 °C[74].

1.6 State of the Art: Cobaltite based cathode

The present scenario of the number of papers published in cathode in the last five years (source: Web of Science, WOS) has been represented in Fig. 1.4. Here, we are representing the data up to June 2021. It means that, during the last five years, most publications have been focused on ferrites. Despite having very much high electrical conductivity and other promising properties, an insignificant number of publications are published in cobaltite. This motivated us to work on the cobaltite-based cathode. In the upcoming section, we will discuss the possible structure for cobaltite cathode.

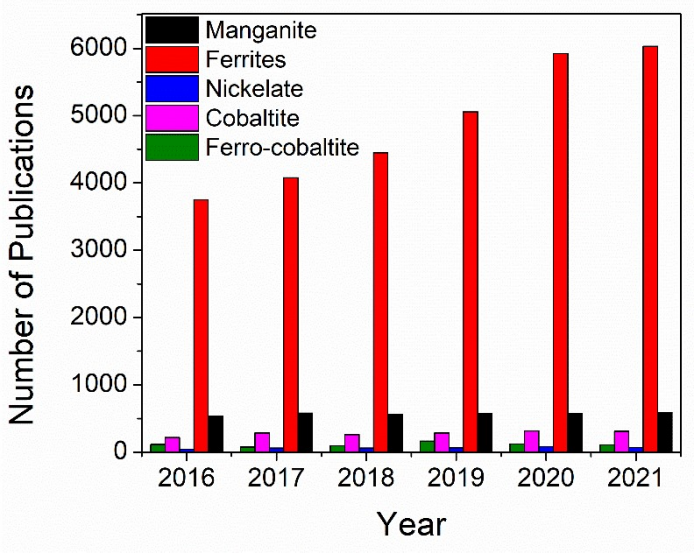

Figure 1.5: Number of publications in the last 5 years the for the keyword of cathode materials

1.6.1 Perovskite structure

Perovskite structure has a general formula unit of ABO_3, where A represents the larger cation with coordination number 12 and B represents the smaller cation with coordination

number 6. In the case of SOFC electrodes, A cation can be alkaline earth metal/rare earth metal, or other whereas B cation can be many transition metals[75]. The ideal structure of perovskite is cubic. The structure deviation of perovskite from its perfect structure is measured in the form of tolerance factor given by the following equation:

$$t = \frac{r_A + r_O}{\sqrt{(r_B + r_O}} \qquad (1.21)$$

The perovskite structure has relatively stable tolerating high-level oxygen vacancy compared to the other structure; therefore, it provides significant oxygen-ion conduction. Octahedral symmetry of oxygen around the reducible transition metal located at B-site provides rapid electron conduction. Therefore, some perovskites are good mixed ionic-electronic conductors (MIEC) and are strong candidates for the cathode materials for SOFC.

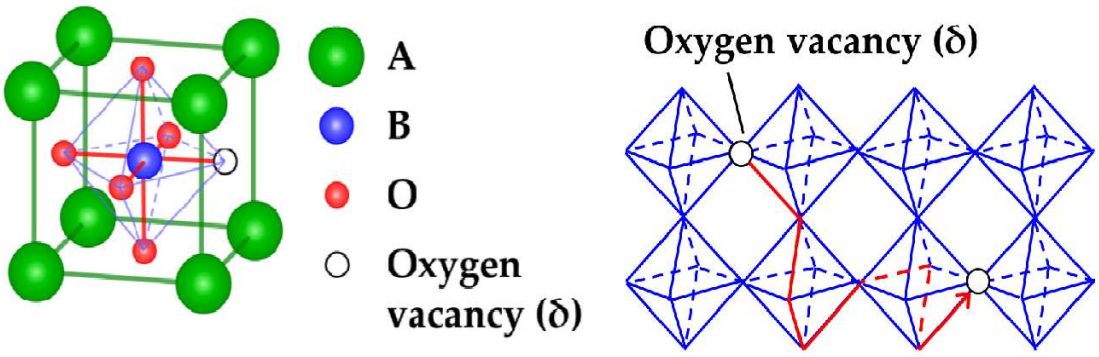

Figure 1.6: (a) Atomic structure in mixed conducting perovskite, left image represents ions' position in a cubic structure, and right image represents the BO_6 octahedra with oxygen vacancy migration path[75]

Among the cobalt-based perovskite oxide, $SrCoO_{3-\delta}$ (SC) is an important parent compound. SC has high oxygen vacancy concentration, beneficial for oxygen ion conduction and ORR on the cathode interface. However, the crystal structure of $SrCoO_{3-\delta}$ is not stable, and the TEC of $SrCoO_{3-\delta}$ is much higher than the traditional electrolyte. In this regard, many

functional materials were developed from SC as a cathode. Lanthanide doped strontium cobalt oxide $Ln_{1-x}Sr_xCoO_{3-\delta}$ (Ln is a rare earth element) has been extensively studied. $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) is a commonly used cathode material. LSC has high electrical properties, catalytic activity, and good thermal stability at an operating temperature[76], [77].

1.6.2 Double Perovskite Structure

Cobaltite-based double perovskite possesses an ordered structure in which A-site sublattice is occupied by lanthanide ion and alkali earth ion. However, the ordering of lanthanide (Ln^{3+}) and alkaline earth (ak^{2+}) ions is favorable only if there is a significant size difference between the A-site cation. Till date, the layered structure is reported only for the barium is used as alkaline earth. The general formula unit of this structure is $LnBaCo_2O_{6-\delta}$. These double perovskites are also known as A-site ordered cobalt perovskite. The ideal structure can be

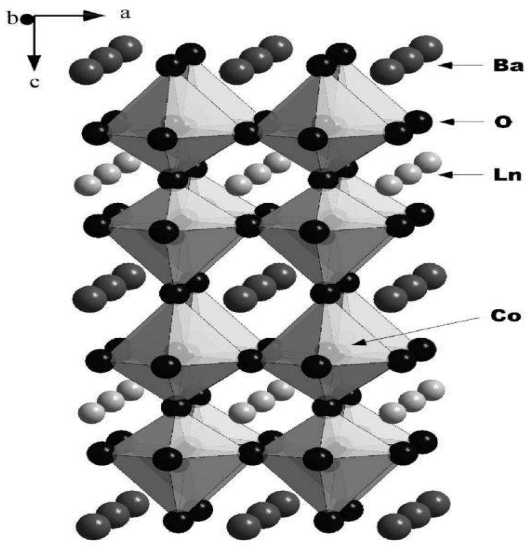

Figure 1.7: Crystal structure of layered perovskite $LnBaCo_2O_{6-\delta}$[78]

represented by the stacking sequence of LnO_{δ}-CoO_2-BaO-CoO_2. This stacking sequence is generated because of the ionic radius difference between the Ba^{2+} ion and Ln^{3+} ion. Oxygen vacancies are localized in the Ln-O plane. This results in the formation of a chain of CoO_5 square pyramids and CoO_6 octahedra[79]. This structure lowers the oxygen-binding strength, offer a disorder-free channel for ion motions, and theoretically increases the oxygen diffusivity by many orders of magnitudes [80].

1.7 Layered perovskite ($LnBaCo_2O_{6-\delta}$)

A-site ordered perovskite 112 types layered structure $LnBaCo_2O_{6-\delta}$ has shown promising MIEC characteristics and ORR activities in recent years. These cobaltite perovskites have the perfect ordering of Ln and Ba ion in alternate layers (001). This is due to the considerable difference in ionic radii of both ions. Another structural property of these cobaltites is the location of oxygen vacancies in Ln layers with a high tendency to form an ordered pattern. This results in the ordered existence of cobalt ions in the pyramidical (CoO_5) or octahedra environment (CoO_6). The first report on these layered perovskite materials was the high oxygen transport rate of $GdBaCo_2O_{6-\delta}$ and found it a suitable candidate for the cathode application. Recent studies have proposed that Ln = Pr and Gd have excellent oxygen transport properties such as high oxygen surface exchange coefficient, high electronic conductivity, and good oxide ion diffusivity[81], [82]. The high mixed conductivity of cobaltite at more elevated temperatures makes these materials appropriate for application, such as oxidation catalysts or materials for the fuel cell.

The layered $LnBaCo_2O_{6-\delta}$ can accommodate a broad range of oxygen vacancies ($0 \leq \delta \leq 1$). However, lower symmetry was observed at $\delta = 0.5$ in vacancy-ordered

$LnBaCo_2O_{5.5}$(orthorhombic with Pmmm symmetry)[83]. Further, increasing or decreasing oxygen vacancy leads to higher symmetry (Tetragonal with P4/mmm).

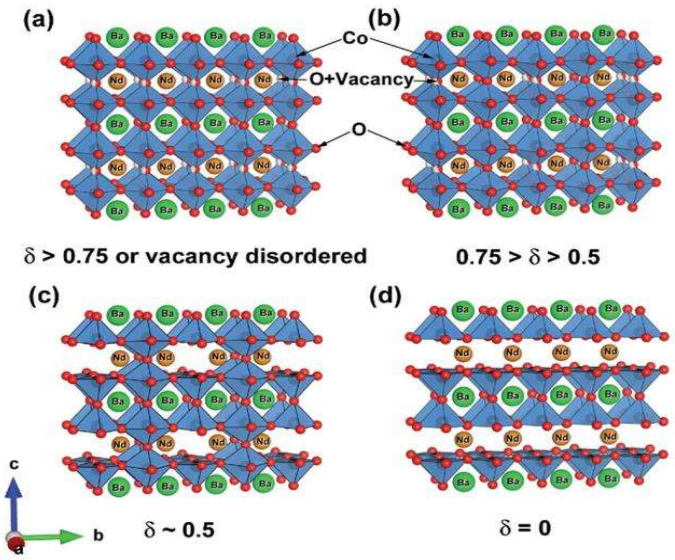

Figure 1.8: Crystal structure of $LnBaCo_2O_{6-\delta}$ (Ln=Nd) at various oxygen content[84]

At room temperature, the crystal structure and the oxygen content of $LnBaCo_2O_{6-\delta}$ are greatly influenced by the A-site cation. The relation between the oxygen vacancy with the difference of size of A-site cation is linear and demonstrated in figure 1.14. However, in the case of the Ln= Pr and Nd, there is a controversy in the room-temperature structure. This is because of the value of δ, which lies around 0.75, where the structural transition arises. At elevated temperature, oxygen loss and reduction in cobalt ion is observed in $LnBaCo_2O_{6-\delta}$. However, the oxygen vacancy amount cannot determine the structure of $LnBaCo_2O_{6-\delta}$ at a high temperature. Rather than, the spin-state transition of cobalt ion and disordering of oxygen vacancies, which are thermally induced, are the factors that influence the crystal structure. Spin state transition of Cobalt ion (Co^{3+}) is observed in several Ln^{3+} ions (Ln= Sm,

Pr, Gd, Nd and Ho) in a temperature range of 0 ^{0}C-200 ^{0}C[85], [86]. This spin state transition leads to the excellent enhancement in electronic conductivity, named as metal-insulator (MI)

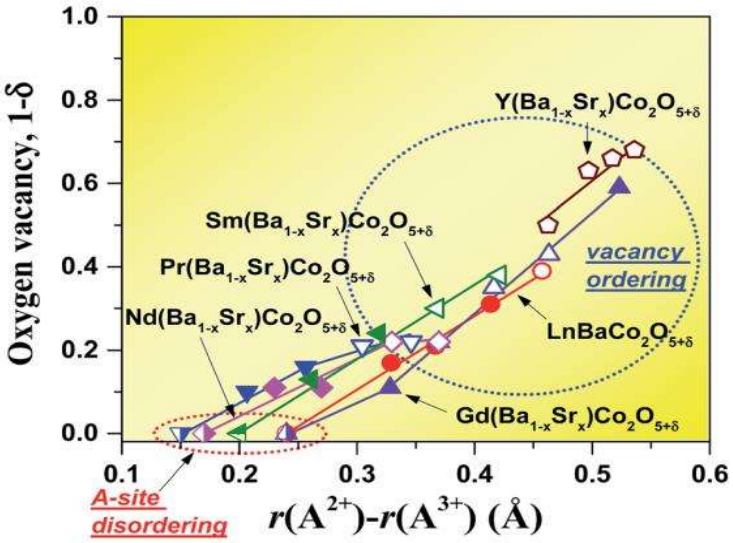

Figure 1.9: Relationship between oxygen-vacancy concentration and A-site cation size differences (rA^{2+}-rA^{3+})(at room-temperature)[87]

Transition. At a higher temperature range (600 ^{0}C-800 ^{0}C), $LnBaCo_2O_{6-\delta}$ observed disordering of oxygen vacancies, beneficial to the oxygen bulk diffusion property[85]. However, this disordering does make any perceptible change in either electronic conductivity or lattice parameter on heating. This makes $LnBaCo_2O_{6-\delta}$ an acceptable choice of cathode materials for IT-SOFC.

At high temperature, $LnBaCo_2O_{6-\delta}$ exhibit superior electronic conductivity. The electronic conductivity for different lanthanides lies in the range of 100 S/cm-1000 S/cm. This metallic conducting behavior is because of the small p-type polaron conducting behavior[88][82]. However, with the increase in temperature, there is an abatement in

electronic conductivity. This is because of the loss of oxygen and reduced charge carrier concentration in $LnBaCo_2O_{6-\delta}$.

$LnBaCo_2O_{6-\delta}$ (Ln= Pr, Sm, Gd, and Ho) also acts as a highly active electrocatalyst for OER in alkaline electrolytes. These perovskites have an O p-band center that lies very close to the Fermi level, which supports the high catalytic activity for OER and the high activities for surface oxygen exchange kinetics upon oxygen reduction[89].

1.7.1 Overview of $PrBaCo_2O_{6-\delta}$

The crystal structure and other fundamental properties of $PrBaCo_2O_{6-\delta}$ (PBCO) have already been discussed in section 1.7. Due to its several unique properties, $PrBaCo_2O_{6-\delta}$ has gained immense research interest among other lanthanide perovskites. At low temperatures (300-500 °C), PBCO has unusual rapid oxygen transport kinetics[90]. Facile oxygen uptake in PBCO powder is observed as low as 200 °C[91]. The surface exchange coefficient and bulk diffusion coefficient for PBCO is about 2-3 times higher than $GdBaCo_2O_{6-\delta}$, which is the most explored material among all lanthanides [92].

$PrBaCo_2O_{6-\delta}$ also has shown excellent potential for application in the cathode of IT-SOFC. The ASR value of the PBCO-GDC composite cathode is reported as low as 0.15 Ω cm^2 at 600 °C in a symmetric cell system[93]. The highest conductivity and maximum power density were accomplished in PBCO compared to other lanthanides in LSGM electrolyte[94]. PBCO has also attracted attention because of its high catalytic activity towards OER. The intrinsic OER activity of PBCO is much higher than various perovskite as $Ba_{0.5}Sr_{0.5}Co_{0.5}Fe_{0.5}O_{3-\delta}$(BSCF), $La_{0.5}Ca_{0.5}Co_5O_{3-\delta}$(LCCO), $LaNiO_3$, $LaCoO_3$, $LaMnO_3$, and also from the metal-based catalyst such as RuO_2 or IrO_2[89].

These all points indicate the potential of PBCO and lead to the fact that PBCO is an exciting compound to carry out the research work.

1.8 The objective of the Present Research Work

The main objective of the present work is to synthesize and investigate the double perovskite PBCO and its composite as air electrodes for fuel cell applications. For this purpose, double perovskite $PrBaCo_2O_{6-\delta}$ has been selected as the parent material. Structural, thermo-dynamical, electrical, and catalytic properties of these materials have been investigated, and the correlation is established. The specific objectives of thesis work are as follows:

1. To synthesize double perovskite $PrBaCo_2O_{6-\delta}$ using various synthesis routes and to investigate the physical and chemical properties, such as structural, microstructural, electrical, electronic properties of the sample PBCO under different optimization condition in order to determine the best optimization conditions for the sample.
2. ORR is the second criteria for the selection of cathode materials after the conductivity and it has been observed that 'A' site ordering and morphology change enhances oxygen ion diffusivity in bulk materials. As a result, second objective is to synthesize a series from PBCO with the variation of element at A-site and investigate its properties for ORR.
3. A-site ordered double perovskites have the potential to act as an OER catalyst as well. As a result, one objective of this work is to synthesize another noble series from the PBCO by altering again the A-site and to study its catalytic behavior for the OER in different medium.

4. Altering the structural features of double perovskite can also impact its catalytic properties. Therefore, one of the objectives of this thesis is to study the behaviour of the best optimized electrode from the above-mentioned series in thin film and to compare the bulk form and nano form of the electrode.

The details of the synthesis process and measurement techniques for studied compounds have been described in the next chapter. The subsequent chapters described the results of the present studied systems.